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Crystallization and Melting Behavior of Poly(ε-caprolactone) under Physical Confinement

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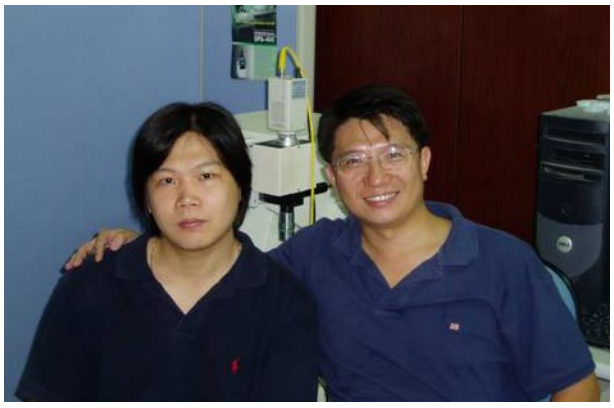
We studied the crystallization behavior of poly(ε-caprolactone) (PCL) in a physically confined system, the self-assembly of poly(ε-caprolactone)/polystyrene-b-poly(ethylenepropylene) (PCL/PS-PEP) blends, using simultaneous small-angle x-ray scattering (SAXS) and wide-angle x-ray diffraction (WAXD). The glassy PS-rich phases effectively confined the PCL crystallization due to the localization behavior of PCL. Contrary to a typical microphase-separated morphology of semi-crystalline copolymers (i.e. a chemically confined system), the physically confined system for the crystallization of PCL provides a representative system for understanding crystallization behavior under spatial confinement. With effective confinement, the crystalline chains of PCL appeared in a random orientation at low crystallization temperatures but in a parallel orientation at high crystallization temperatures.

Crystallization behavior under nanoscale confinement has drawn attention due to the necessity of having a basic understanding of crystallization in order to develop nanotechnology applications. In particular, the crystallization behavior of semi-crystalline block copolymers, in which at least one of the constituted blocks is crystallizable, has been thoroughly studied as illustrated in **Figure 1a** (namely, a chemical confinement). By contrast, the unique morphology with a crystallizable PCL component localized between the lamellar microdomains of PS-PEP gives rise to a specific crystallization environment in which the crystallization is carried out in a nanometer-scale confined environment without the restraint of a chemical connection (**Figure 1b**, a physical confinement). This unique morphology, a crystallizable PCL component localized favorably within PS-rich constituted lamellar in a PS-PEP block copolymer, has been obtained via melt-mixing in a MiniMax mixer. Shear (velocity), vorticity, and velocity gradient directions are labeled *x*, *y*, and *z*, respectively. Two-dimensional SAXS patterns along the *x*, *y*, and *z* directions indicate that microphase-separated microdomains can be oriented after melt-mixing, as illustrated in **Figure 2** for PCL11/PS-PEP blends (the M_w of PCL11 is 11000g/mol). Up to four orders of lamellar scattering peaks (q/q* = 1 : 2 : 3: 4) can be identified when the incident x-ray beams are along *x* and *y*, as shown in **Figure 2a-2b**. By contrast, we found no significant scattering peak along the *z* direction in the two-dimensional SAXS pattern (**Figure 2c**). These two-dimensional SAXS results indicate that microphase-separated lamellae of PCL11/PS-PEP are aligned parallel to the x-y plane (i.e. the shear plane). Moreover, the oriented microphase-separated lamellar microstructure was preserved after PCL crystallization so that the PCL is completely confined in the PS-PEP lamellar layer.

For PCL crystallization at low crystallization temperatures (for instance, at T_c= -20°C), the two-dimensional WAXD patterns exhibit a typical ring pattern in all directions, suggesting that PCL crystals appear randomly oriented under confinement. However, a specific orientation of the PCL crystals can be identified when the shear-aligned samples are crystallized at high crystallization temperatures (for instance, 40°C). Two-dimensional WAXD patterns along the *x* and *y* directions are practically identical, and exhibit oriented features (**Figure 2d-2e**). Only an isotropic ring pattern along the *z* direction was observed (**Figure 2f**). On the basis of the orthorhombic lattice structure of PCL crystals with a unit cell of a=0.749nm,



Yeo-Wan Chiang (left) and Rong-Ming Ho

b=0.498nm, c=1.703nm, and $\alpha = \beta = \gamma = 90^{o}$, the corresponding reflections were identified as {110} and {200}. The azimuthal profiles (**Figure 3a**) were obtained from the two-dimensional WAXD pattern (**Figure 2d**). The intense {110} diffraction peaks are separated into four diffraction arcs and appear at $\Phi=56^{o}$, 124^{o}, 236^{o}, and 304^{o}, and two {200} reflections appear at $\Phi=0^{o}$, 180^{o}, respectively. According to the azimuthal results, the diffraction pattern is illustrated in **Figure 3b**. The fiber-pattern-like diffractions suggest a parallel-type orientation with PCL crystalline chains parallel to the microphase-separated lamellae (i.e. the *x* and *y* directions). **Figure 3c** shows the molecular disposition of crystalline PCL chains, and indicates their parallel orientation at high crystallization temperatures in a physically confined environment. The crystalline orientation is strongly dependent upon the crystallization temperature under physical confinement. As a result, the orientation of the PCL crystalline chain localized between the PS-PEP layers can be thoroughly understood by two-dimensional SAXS and WAXD techniques at a synchrotron light source.

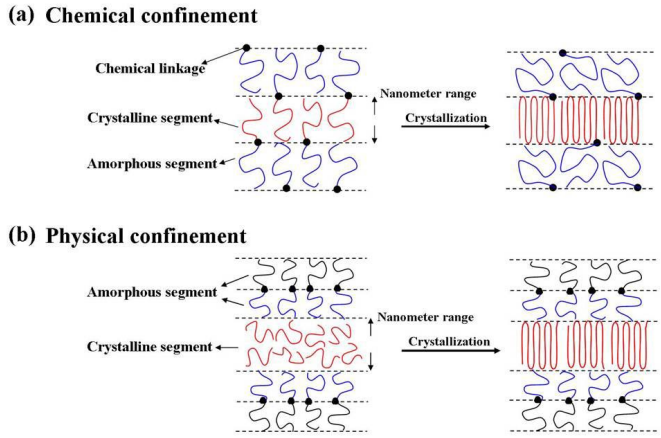


Figure 1. *Schematic pictures of (a) chemical confinement and (b) physical confinement.*

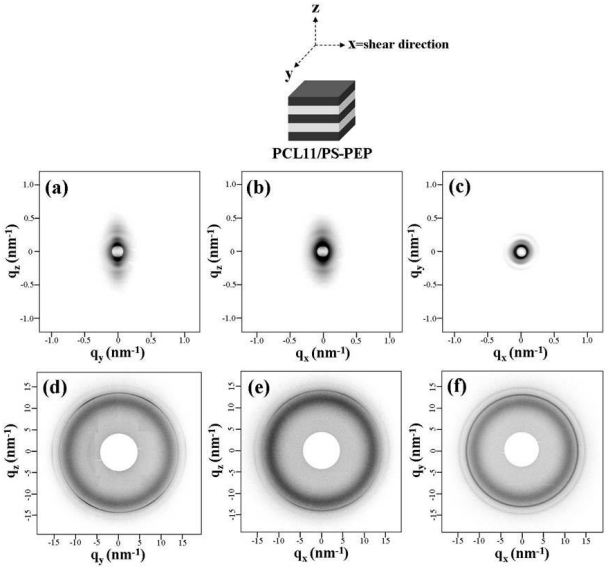


Figure 2. *Simultaneous SAXS and WAXD patterns of orientated PCL11/PS-PEP samples isothermally crystallized at 40°C from ordered melt at 100°C. 2D SAXS (above) and 2D WAXD (below) obtained (a) along the x-direction, (b) along the y-direction, and (c) along the z-direction.*

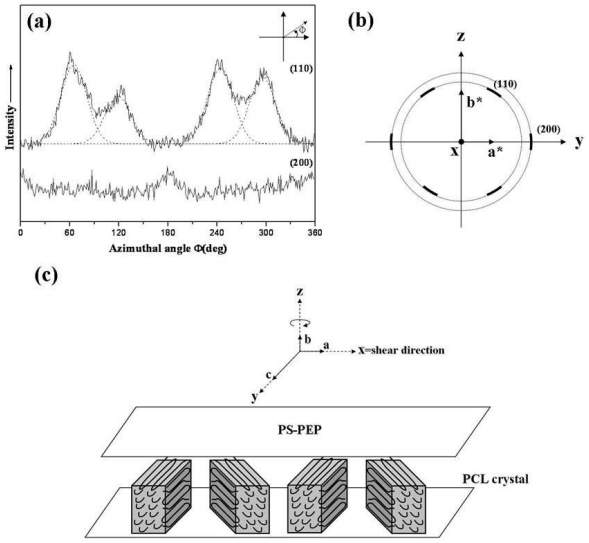


Figure 3. *(a) Azimuthal scanning profiles of the {110} and {200} reflections of the WAXD patterns in Figure 2d for the PCL11/PS-PEP blends isothermally crystallized at 40 °C. (b) Schematic diagram of the WAXD pattern with indexed reflections. (c) Schematic diagram of the microstructure of oriented PCL11/PS-PEP samples isothermally crystallized at 40°C from ordered melt at 100°C. The crystallization of PCL is confined between the preformed lamellar PS layers, and the a and c axes of the PCL crystals are preferentially parallel and perpendicular to the axes of the PS lamellar normal, respectively.*